Indian J. Phys. **65A** (4), 293-299 (1991)

Thermal oxidation study of natural tourmaline using Mossbauer effect

H V Varma

Deparment of Physics, Dr. H. S. G. University, Sagar-470 003, India

Received 25 September 1990, accepted 8 April 1991

Abstract: Minerals having hydroxyl group show conversion of ferrous ions to ferric ions when heated in air. Several mechanisms have been suggested for this process of conversion of ferrous to ferric. One mechanism which has been suggested is the hopping mechanism of electron-proton pair. In the case of tourmaline, using the thermal oxidation and the technique of Mossbauer effect it has been confirmed that the hopping mechanism is responsible for the oxidation. The oxidation of ferrous ion takes place by the ejection of the natural atom of hydrogen rather than a proton-electron pair. This natural atom of hydrogen hops to the surface of the sample and oxidizes with atmospheric oxygen to form water.

Keywords: Mossbauer effect, tourmaline oxidation, thermal oxidation, natural mineral.

PACS No: 76.80.+y

1. Introduction

Iron bearing minerals having hydroxyl group show conversion of ferrous ions to ferric ions when heated in air. Vedder and Wilkins (1969) and Hogg and Meads (1975) have suggested that ferrous ions coordinated by oxygen and hydroxyl ions when heated, oxidise to ferric ion coordinated by one less hydroxyl. The hydrogen atom released in this process diffuses to the surface of the material and oxidises with atmospheric oxygen to form water. A hopping mechanism of proton-electron pair has been suggested by Pollak and Bruyneel (1975) and Danon *et al* (1976). Bhandari and Varma (1976) have studied thermal oxidation of the ferrous ions in tourmaline and observed that in vacuum heating the conversion of ferrous to ferric is slowed down to a great extent. The present paper reports the results of the thermal oxidation done on tourmaline and studied using Mossbauer effect.

Tourmaline is a mineral of granite and occurs in some metamorphic rocks as a mineral in sediments. It is a cyclosilicate and is built around SiO(4) tetrahedra and has a ratio of Si : O = 1 : 3. In addition to Si(6)O(18) rings, there are independent BO(3) triangles and OH groups in its structure. All these structural

units are bound together by ionic bonds through x- and y-type cations where x-type cations are sodium and calcium and y-type are magnesium, ferrous iron, aluminum, ferric iron, divalent manganese and lithium. The iron ions are surrounded octahedrally by oxygen and OH ions. The three octahedra immediately surround the 3-fold axis at the origin and each octahedron shares an edge with each of its two equivalent neighbours.

Scorezelli *et al* (1976) resolved the Mossbauer spectrum of tourmaline in two $Fe(2^+)$. These authors found $Fe(3^+)$ to be less than 1% and observed the linewidths to be 0.36 mm/sec for outer doublets and 0.6-0.7 mm/sec for inner doublets. Saegusa *et al* (1979) resolved the Mossbauer spectrum of tourmaline in four doublets and assigned them to two $Fe(2^+)$ doublets, one $Fe(3^+)$ doublet and one doublet to neighbouring $Fe(2^+) \leftrightarrow Fe(3^+)$ pairs between which there is a fast electron hopping. The Mossbauer spectrum of tourmaline has been assigned to four doublets by Belov *et al* (1973) where these authors assigned two doublets to ferric sites —one with trans-OH site and the other with cis-OH site and the other two quadrupole doublets to two ferrous sites. Bhandari and Varma (1976) on the basis of the thermal oxidation study in air assigned two ferrous doublets and two ferric doublets.

In a powdered sample, the hopping mechanism can be studied if the amount of oxidation can be changed. It is expected that there should be a substantial decrease in the rate of oxidation as the size of the grain is increased in a polycrystalline powder. Further, this fall in the rate of oxidation should tell us about the way the electron-proton pair or hydrogen atom migrates to the surface. Using a similar argument one should be able to observe the effect of heating a sample of particular grain size at a fixed temperature for different durations. In this case the energy imparted to the atom at a particular temperature of heating will give a finite probability of crossing barrier by the electron-proton and causing oxidation with increase of heating durations.

2. Experimental method

A natural crystal of black tourmaline was taken and was powdered. The untreated powder was sieved through different meshes of sizes 60, 85, 150 and 110 microns. The powders were heated in air at temperatures 950, 1000 and 1050 K for various durations. The powders were allowed to cool to room temperature and the Mossbauer spectra were recorded in the transmission geometry using absorbers of these samples. The source used in these studies was a Co-57 in palladium matrix. Calibration was done using a thin natural iron foil.

3. Results and discussion

The Mossbauer spectrum of powdered natural tourmaline is shown in Figure 1. The spectrum is resolved into four doublets. Two doublets *A* and *C* correspond to ferric iron and two doublets *B* and *D* correspond to ferrous iron. The vertical

lines represent the intensity and peak positions of the various doublets. The spectra were computer fitted using a non-linear variable matrix minimization

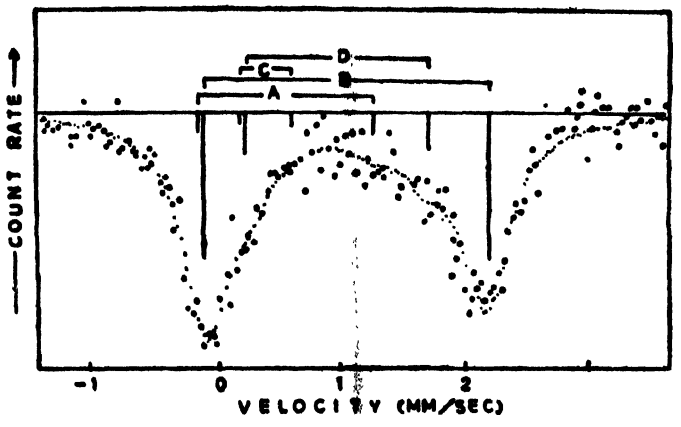

Figure 1. Mossbauer spectrum of powdered sample of tourmaline. Vertical lines show the peak intensity. The four quadrupole split doublets are *A*, *B*, *C* and *D*.

technique (Meerwall 1975, Davison 1959). The constraints of equal widths for all the peaks and equal intensity for the two peaks of the same doublet were not

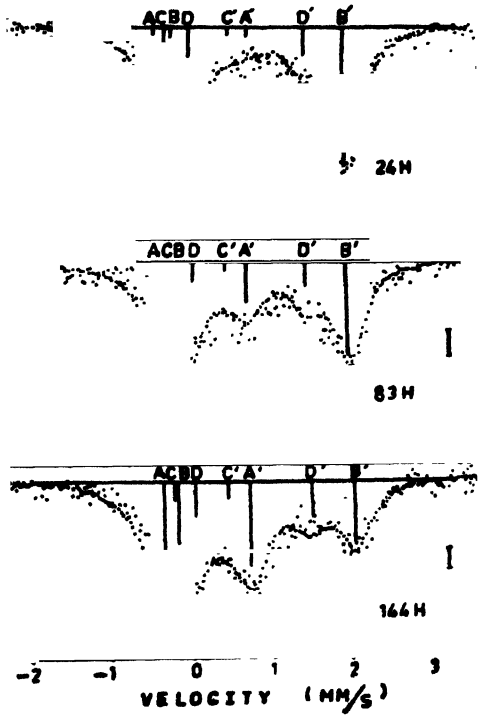

Figure 2. Mossbauer spectra of tourmaline of 110 micron size heated at 950K for different durations.

released during the fit. The value of the chisquared per degree of freedom was well below 2 and was taken to be acceptable. The Mossbauer spectra obtained for grain size of 100 microns and heated at 950K for different durations are shown in Figure 2. Similar spectra were recorded and computer fitted for other grain sizes and for different temperatures of heating and different durations. The grains were found to be nearly spherical when observed under a magnifying glass.

The different parameters obtained from the fittings are shown in Table 1. It is observed that as the sample is heated for different durations, the percentage of

Table 1. Table showing the values of ϵ obtained for tourmaline mineral powder of different grain sizes.

Grain size (microns)	ϵ (Electron volts)
60	3.55
85	1.87
110	2.25
150	2.17 (36)

$Fe(2^+)$ goes on decreasing. The variation of the intensity of total $Fe(2^+)$ with durations of heating for different grain size at 950K is shown in Figure 3. Similar

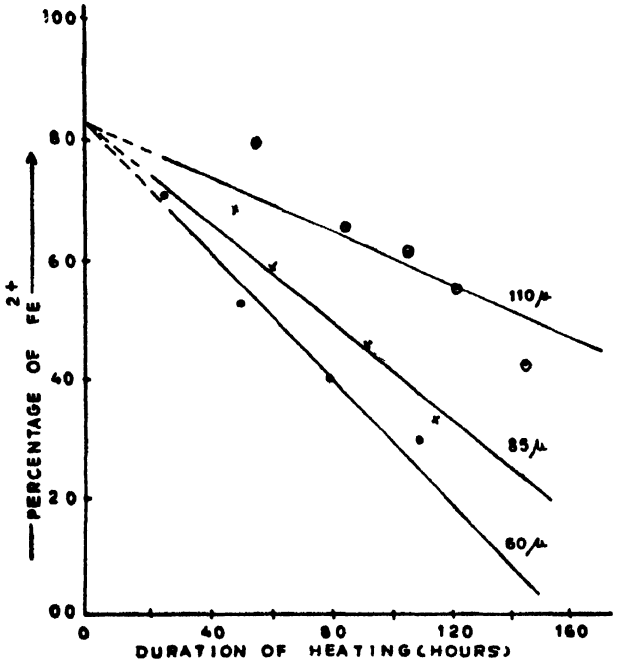

Figure 3. Variation of $Fe(2^+)$ (percentage of total iron) with duration of heating for different grain size powders of tourmaline at 950K.

curves were plotted for different temperatures of heating. One observes that the rate of oxidation goes on increasing as the grain size is reduced. It was also observed that the rate of oxidation goes on increasing as the temperature is increased.

The slopes of the lines from Figure 4 and similar curves for different temperatures of heating were calculated. Logarithms of the slopes versus reciprocal of

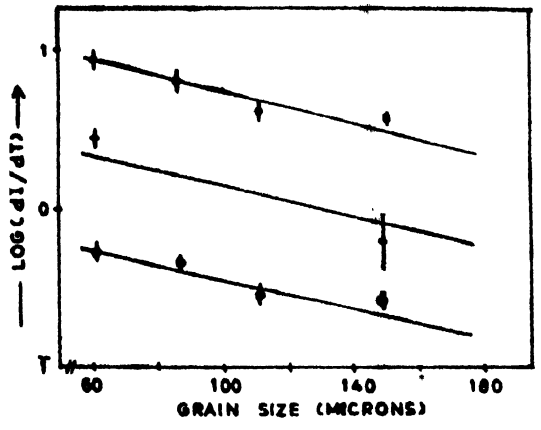

Figure 4. Variation of log $(\partial I/\partial t)$ of Fe(2⁺) with grain size at different temperature of heating.

temperature in Kelvin, when plotted, gave the graph as shown in Figure 5. It is observed that the slopes of all of them are nearly same, within experimental errors.

For the total intensity of $Fe(2^+)$ we write

$$I(t, x, T) = I(0) - Af(t, x, T) \tag{1}$$

where $I(t, x, T)$ is the total intensity of $Fe(2^+)$ present in a sample which is of grain size x, heated at a temperature T for a duration t. $I(0)$ being the amount of $Fe(2^+)$ initially present in a particular sample. A is a constant which among other things depends on the efficiency of detection of $Fe(2^+)$ and the f-values for $Fe(2^+)$ and $Fe(3^+)$. $f(t, x, T)$ is a function of t, x, T.

With the help of graphs shown in Figures 3 to 5 we obtain the relation (1) to be written more precisely as (Varma 1984, Varma 1982)

$$I = I(0) - A.t.\exp(-\alpha x)\exp(-\epsilon/kT) \tag{2}$$

where α and ϵ are constants and k is the Boltzmann constant.

Differentiating eq. (2) partially with respect to time t we obtain

$$\partial I/\partial t = -A\exp(-\alpha x)\exp(-\epsilon/kT) \tag{3}$$

which on taking logarithms of both sides gives

$$\ln(\partial I/\partial t) = -\ln A - \alpha x - \epsilon/kT \tag{4}$$

or

$$\ln(\partial I/\partial t) = -\epsilon/kT - (\ln A + \alpha x) \quad (5)$$

If we plot ln $(\partial I/\partial t)$ versus $1/T$ we obtain a straight line from eq. (5) and its slope gives ϵ/k. Curves of Figure 5 are used to determine the value of ϵ/k. The values of ϵ are tabulated in Table 1 where the values of ϵ are in electron volts.

The oxidation mechanism has been associated with the hydrogen migration from the hydroxyl group through the lattice to the surface either as a hydrogen

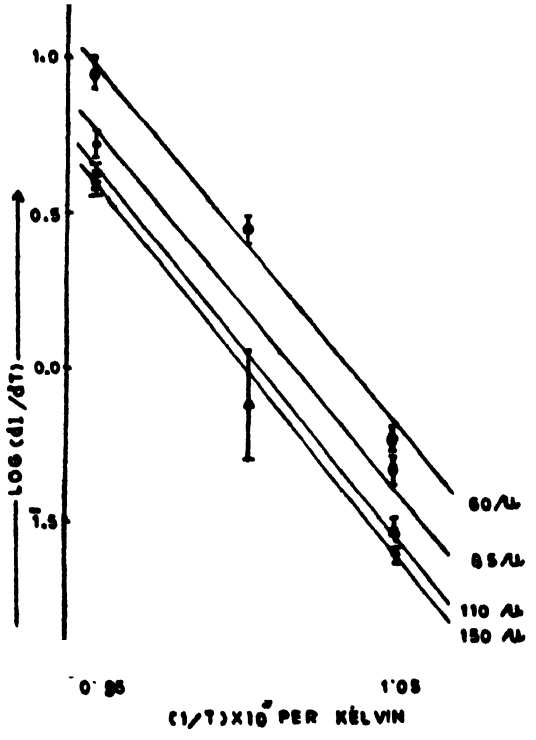

Figure 5. Variation of log $(\partial I/\partial t)$ of Fe(2+) with reciprocal of temperature of heating for different grain sizes.

atom or as an electron-proton pair. In either case hydrogen had to traverse some sort of an average distance before reaching the surface of the grain. This average distance is some fraction of the grain size x. It is difficult to estimate this average distance as it would depend on the exact shape of the grain which could vary from spherical in the simplest case to cylindrical in the extreme case. All one can say is that the average distance could be related to the overall grain size x.

The constant in the eq. (2) where k is the Boltzmann constant can be interpreted as the barrier height or the binding energy of the hydrogen atom in the hydroxyl group. The value of the binding energy of an H(+) ion in the OH group

is 5 eV (Uri 1952) and the binding energy of the H atom in HO – O is 2-2.5 eV (Evans and Uri 1949, Swarc 1948, Walsch 1948). The value of the binding energy favours the idea that the oxidation of ferrous ions takes place by the ejection of the natural atom of hydrogen rather than a proton-electron pair. The hydrogen atoms which survive the capture by another ferric ion are able to reach the surface and get oxidised.

References

Belov V F, Khimich T A and Kolesnikov I M 1973 *Dokl. Akd. Nauk SSSR* **209** 922
Bhandari S S and Varma J 1976 *Nucl. and Solid State Phys. Symp. Proc.* (Calcutta, India)
Danon J, Scorzelli R B and Baggio-Saitovitch E 1976 *Corfu Conference Proc.* 801
Davison W 1959 *AEC R and D Report ANL* 5990
Evans M G and Uri N 1949 *Trans. Faraday Soc.* **45** 224
Hogg C S and Meads R E 1975 *Min. Mag.* **40** 79
Meerwall E M von 1975 *Comp. Phys. Commun.* **9** 117
Pollak H and Bruyneel W 1975 *Int. Conf. on Mossbauer Spec. Proc.* I 427
Saegusa N, Price D C and Smith G 1979 *J. de Phys.* **40** C2-456
Scorezelli R B, Baggio-Saitovitch E and Danon J 1976 *J. de Phys. Colloq.* **37** C6-801
Swarc M 1948 *J. Chem. Phys.* **16** 128
Uri N 1952 *Chem. Rev.* **50** 375
Varma H V 1982 *Nucl. and Solid State Phys. Symp. Proc.* (Varanasi, India)
——1984 *Ph. D. Thesis* (Sukhadia University, Udaipur, India)
Vedder W and Wilkins R W T 1969 *Amer. Min.* **54** 482
Walsch A D 1948 *J. Chem. Soc.* 331